A new family of N_xO_y pyridine-containing macrocycles: Synthesis and characterization of their Y(III), Ln(III), Zn(II), and Cd(II) coordination compounds

Carlos Lodeiro, Rufina Bastida, Emilia Bértolo, and Adolfo Rodríguez

Abstract: Reaction between 2,6-bis(2-formylphenoxymethyl)pyridine and *N*,*N*-bis(3-aminopropyl)methylamine or tris(2-aminoethyl)amine has been used as the starting point for the synthesis of seven oxa-aza macrocyclic ligands, five of them never reported previously. They all feature different pendant arms, which provide a wide range of coordination possibilities. The Schiff base macrocycles L^1 and L^4 and their reduced ligands L^2 and L^5 are derived from 2,6-bis(2-formylphenoxymethyl)pyridine and tris(2-aminoethyl)amine or *N*,*N*-bis(3-aminopropyl)methylamine, respectively. The reaction of L^1 with salicylaldehyde forms L^3, which features an imine bond in the pendant arm. The ligand L^5 has been the precursor for the pendant-armed L^6 and L^7, by alkylation of the free NH groups with methyl-imidazole or methyl-indole. By a template or a nontemplate approach, we have synthesized different mono- and dinuclear complexes with Y(III), Ln(III), Zn(II), and Cd(II) cations. Both the free macrocyclic ligands and their corresponding metal complexes have been characterized by microanalysis, IR, UV–vis, ^{1}H and ^{13}C NMR spectroscopy, FAB mass spectrometry, MS electrospray, and conductivity measurements.

Key words: Schiff-base macrocycle, template synthesis, macrocyclic ligand complexes, lanthanide(III) complexes.

Résumé : On a utilisé la réaction de la 2,6-bis(2-formylphénoxyméthyl)pyridine avec la *N*,*N*-bis(3-aminopropyl)méthylamine ou la tris(2-aminoéthyl)amine comme point de départ pour la synthèse de sept ligands oxa-aza macrocycliques, dont cinq n'avaient pas été rapportés antérieurement. Ils comportent tous des bras pendants différents qui peuvent donner lieu à des possibilités différentes de coordination. Les macrocycles à base de bases de Schiff, L^1 et L^4, ainsi que leurs ligands réduits, L^2 et L^5, sont dérivés respectivement de la 2,6-bis(2-formylphénoxyméthyl)pyridine et de la tris(2-aminoéthyl)amine ou de la *N*,*N*-bis(3-aminopropyl)méthylamine. La réaction du ligand L^1 avec le salicylaldéhyde conduit à la formation du ligand L^3 qui comporte une liaison imine dans le bras pendant. Le ligand L^5 est le précurseur des ligands L^6 et L^7 à bras pendant par l'alkylation des groupes NH libres à l'aide de méthyl-imidazole ou de méthyl-indole. Utilisant des approches avec ou sans gabarit, on a réalisé la synthèse de différents complexes mono- et dinucléaires comportant dans cations Y(III), Ln(III), Zn(II) et Cd(II). On a caractérisé les ligands macrocycliques libres ainsi que leurs complexes métalliques correspondants par microanalyse, spectroscopies IR, UV–vis et RMN du ^{1}H et du ^{13}C, par spectrométrie de masse par bombardement avec des atomes rapides (FAB) ou par ionisation par électronébulisation.

Mots clés : base de Schiff macrocyclique, synthèse à l'aide de gabarit, complexes de ligands macrocycliques, complexes de lanthanide(III).

[Traduit par la Rédaction]

Introduction

Pyridine-containing macrocycles have always attracted considerable interest because of their versatility. They can be used as building blocks that lead to more complicated structures, including systems with more than one cavity, three-dimensional cages, and ligands with additional functional groups attached to the macrocyclic skeleton (1–7). Some macrocycles involving *N*-methyl-pyridine, *N*-methyl-indole, or *N*-methyl-imidazole have been prepared and their coordination ability towards divalent and trivalent metal anions evaluated (8–11).

The synthesis of new receptors with pendant arms that have aromatic or aliphatic units is a fascinating area of research because of the importance of these receptors both in basic and applied chemistry. A subject of special interest is

Received 18 September 2003. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 16 February 2004.

C. Lodeiro,[1,2] R. Bastida, E. Bértolo, and A. Rodríguez. Departamento de Química Inorgánica. Universidad de Santiago de Compostela. Avda. das Ciencias s/n. 15782 Santiago de Compostela, Galicia, Spain.

[1]Present address: REQUIMTE-CQFB, Departamento de Química, Faculdade de Ciências e Tecnología, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Monte de Caparica, Portugal.
[2]Corresponding author (e-mail: lodeiro@dq.fct.unl.pt).

 doi: 10.1139/V03-214

the design of homo- or hetero-binuclear complexes for biomedical applications that require covalent attachment of the macrocycle system to a recognition site (12–16). Cytotoxic studies of transition metal ion concentrations (i.e., copper(II), zinc(II), and cadmium(II)) have also been carried out using macrocyclic ligands with pendant arms (17, 18). Lanthanide(III) ions have been employed as effective template agents (19, 20) in the synthesis of large macrocycles with pyridine head units.

In the present work, we describe the synthesis and characterization of a new group of oxa-aza macrocyclic ligands containing a pyridine head and phenyl lateral units (see Fig. 1). The heptadentate Schiff base macrocycle L^1 and its corresponding reduced ligand L^2 are derived from the reaction between 2,6-bis(2-formylphenoxymethyl)pyridine (**I**) and tris(2-aminoethyl)amine. Both macrocycles have a flexible amine pendant arm, with potential to form new macrocyclic ligands by condensation with different carbonylic species. Very recently we have reported a related compound of ligand L^1 (21). In those cases the stability of the complexes was increased by coordination of the flexible amine pendant arm to the metal ions. In this work, we present the reaction of L^1 with salicylaldehyde to form L^3, which features an imine bond. The Schiff base ligand L^4 has been obtained by reaction between 2,6-bis(2-formylphenoxymethyl)pyridine and *N*,*N*-bis(3-aminopropyl)methylamine and subsequently reduced to obtain L^5. The ligand L^5 has been the precursor for the pendant-armed macrocycles L^6 and L^7 by alkylation reaction of the NH groups with methylimidazole or methyl-indole. This thus covalently introduces a biological substrate in the macrocycle skeleton. We have studied the coordination capability of the macrocyclic ligands towards different metallic ions. We report the synthesis of the corresponding homodinuclear or mononuclear Y(III), Ln(III), Zn(II), and Cd(II) complexes, using nitrate or perchlorate as the counter ions. Both a direct route and a template approach have been used as required.

Experimental section

Methods

Elemental analyses were performed by the University of Santiago de Compostela Microanalytical Service in Carlo Erba 1108 and Leco CNHS-932 microanalysers. Infrared spectra were recorded as KBr discs or in CsCl windows, using a Mattson Cygnus 100 spectrophotometer. Proton and carbon NMR spectra were recorded using a Bruker WM-300. Positive ion FAB mass spectra were recorded on a Kratos MS50TC spectrometer, using 3-nitrobenzyl alcohol (MNBA), glycerol, or 2-hydroxyethyl disulfide matrixes. Electrospray mass spectra were recorded using acetonitrile and acetic acid mixture as solvent. Melting points were carried out using a BÜCHI melting point apparatus. Conductivity measurements were carried out in 10^{-3} mol dm^{-3} acetonitrile or DMF solutions at 25 °C using a WTW LF-3 conductivimeter. The electronic absorption spectra of some complexes and ligands (MeCN solutions) were measured in the 220–850 nm range using a PerkinElmer Lambda 6 spectrophotometer, and the fluorescence emission spectra of the Eu(III), Tb(III), and Zn(II) complexes were measured on a SPEX F111 Fluorolog spectrofluorometer.

Chemicals and starting materials

2,6-Bis(2-formylphenoxymethyl)pyridine was prepared according to the method reported by Fenton and co-workers (22). *N*,*N*-bis(3-aminopropyl)methylamine and tris(2-aminoethyl)amine, Y(III), Ln(III), Zn(II), and Cd(II) metal nitrates and perchlorates were commercial products from Alfa and Aldrich and were used without further purification. Salicylaldehyde was a commercial product from Carlo Erba. 5-Chloromethyl-4-methylimidazole hydrochloride and 3-chloromethylindole were synthesized according to the literature method (23). Solvents were of reagent grade and were purified by the usual methods. The synthesis of the free imine macrocyclic ligands L^1 and L^4 has been reported in a previous paper (24). Caution: Perchlorate salts are potentially explosive.

Synthesis of the reduced macrocycles L^2 and L^5

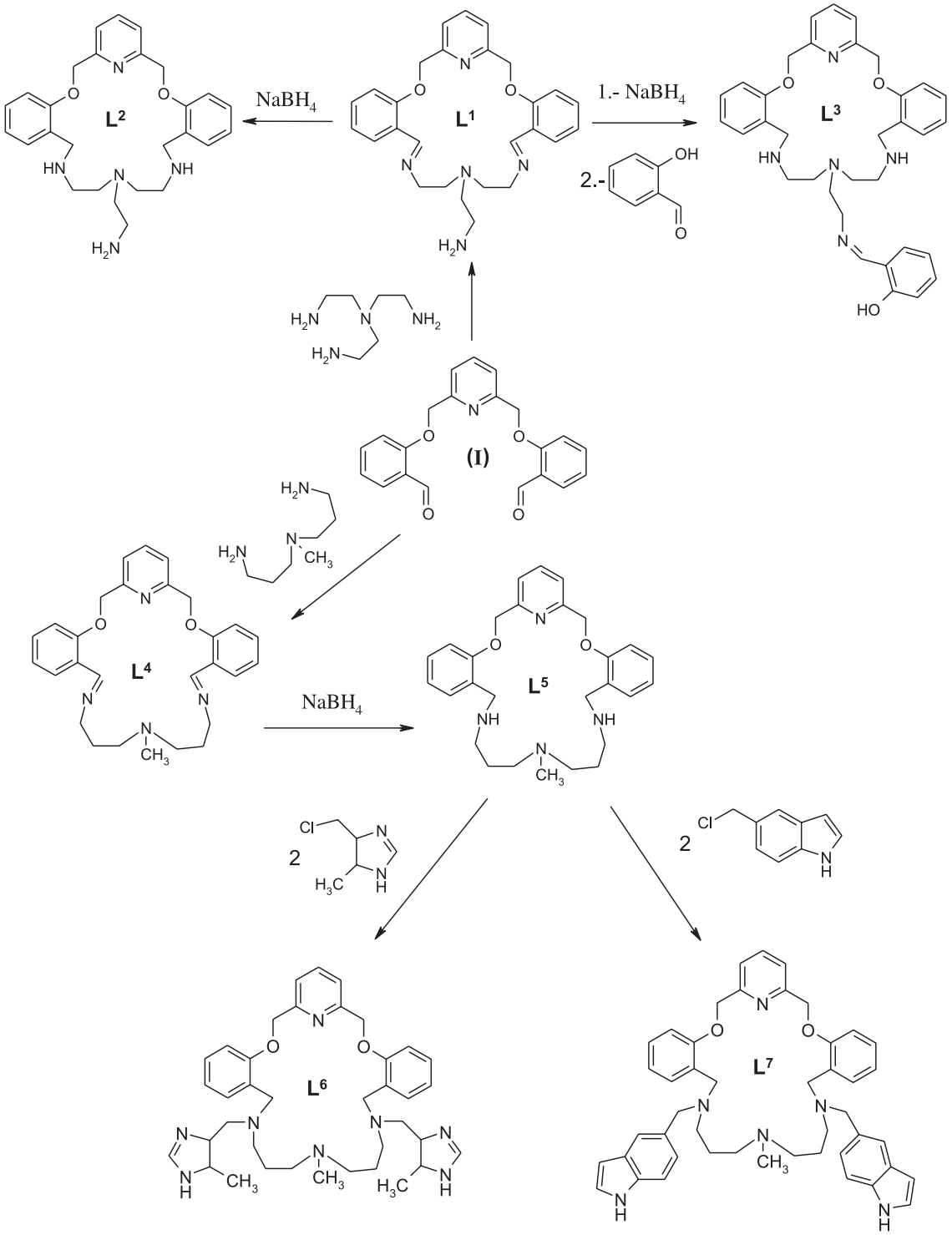
The two ligands were prepared by a modification of the method reported in refs. 22 and 25. The corresponding aliphatic polyamine (4.0 mmol) in warm solvent (100 cm^3) was slowly added to a solution of 2,6-bis(2-formylphenoxymethyl)pyridine (4.0 mmol) and $Ba(ClO_4)_2{\cdot}xH_2O$ (4.0 mmol) in warm solvent (300 cm^3). The reaction mixture was refluxed for 6 h, allowed to cool down, and then put in an ice bath. Solid $NaBH_4$ (55.0 mmol) was added carefully in solid incremental amounts, with stirring. After the effervescence stopped, a white precipitate was removed by filtration. The filtrate was reduced to dryness by rotary evaporation, and chloroform (150 cm^3) was added; the resulting solution was then stirred for ca. 72 h. A grey precipitate was removed by filtration; the filtrate was then dried over anhydrous sodium sulphate, and subsequently the sodium sulphate was removed by filtration. The filtrate was concentrated to ca. 10–15 cm^3 and diethyl ether was added, producing the product, which was filtrated (L^2) or decanted (L^5) and dried in vacuo.

L^2

Yellow solid. Amine: tris(2-aminoethyl)amine. Solvent: methanol. Yield 64%. Melting point: 195–200 °C. IR (KBr disc) ν(NH) (cm^{-1}): 3200; ν(NH_2) (cm^{-1}): 3064, ν(C=C) and ν(C=N) (cm^{-1}): 1597, 1453. UV–vis spectrum (in CH_3CN) (λ(mn), ε((mol L^{-1})$^{-1}$·cm^{-1}): 269, 5344. ^{1}H NMR (CD_3CN) (ppm) δ: 8.6 (t), 1H, (Py); 8.3 (d), 2H, (Py); 7.6 (d) 2H, (C_6H_6); 7.5 (t), 2H, (C_6H_6); 7.3 (d), 2H, (C_6H_6); 7.1(t), 2H, (C_6H_6); 5.6(s), 4H, (Py-CH_2-O); 4.4(s), 4H, (Ph-CH_2-NH); 3.6–3.2(m), 12H, (-CH_2CH_2); 5.00(sw), (-N*H*). ^{13}C NMR (CD_3CN) (ppm) δ: 156.8, 156.0, 155.4, 137.6, 131.2, 130.3. 129.2, 128.7, 128.1, 127.7, 127.1, 126.1, 122.6, 121.9, 120.6, 112.7, 112.1, 97.1, 71.3, 61.7, 54.1, 53.3, 48.3, 47.8, 47.0, 45.6, 44.3. FAB-MS (positive-ion) *m*/*z*: 462 ([L^2 + H]$^+$). Anal. calcd. for $C_{27}H_{35}N_5O_2{\cdot}3.5H_2O$ (%): C 61.85, H 8.05, N 13.30; found: C 61.50, H 7.95, N 12.50.

The ligand is air stable and soluble in acetonitrile, absolute ethanol, chloroform, dimethylformamide, and dimethylsulfoxide; it is moderately soluble in dichloromethane and insoluble in diethyl ether, petroleum ether, and water.

Fig. 1. Schematic diagram showing the synthetic route to obtain the different ligands. **L[1]**: 2-[3.25-dioxa-11.14.17.31-tetrazatetracyclo-[25.3.1.O$^{4.9}$.O$^{19.24}$]hentriaconta-1(31).4(9).5.7.10.17.19(24).20.22.27.29-undecaen-14-yl]-1-ethanamine. **L[2]**: 2-[3.25-dioxa-11.14.17.31-tetrazatetracyclo[25.3.1.O$^{4.9}$.O$^{19.24}$]hentriaconta-1(31).4(9).5.7.10.17.19(24).20.22.27.29-nonaen-14-yl]-1-ethanamine. **L[3]**: 2-[({2-[3.25.dioxa-11.14.17.31-tetraazatetracyclo[25.3.1.O$^{4.9}$.O$^{19.24}$]hentriaconta-1(30).4(9).5.7.19(24).20.22.27(31).28-nonaen-14-yl]ethyl}imino)methyl]phenol. **L[4]**: 15-methyl-3.27-dioxa-11.15.19.33-tetraazatetracyclo[27.3.1.O$^{4.9}$.O$^{21.26}$]tritiaconta-1(32).4(9).5.7.10.19.21(26).22.24.29(33).30-undecane. **L[5]**: 15-methyl-3.27-dioxa-11.15.19.33-tetraazatetracyclo[27.3.1.O$^{4.9}$.O$^{21.26}$]tritiaconta-1(32).4(9).5.7.10.19.21(26).22.24.29(33).30-nonaene. **L[6]**: 15-methyl-11.19-di[(5-methyl-1*H*-4-imidazolyl)methyl]-3.27-dioxa-11.15.19.33-tetraazatetracyclo[27.3.1.O$^{4.9}$.O$^{21.26}$]tritiaconta-1(32).4(9).5.7.21(26).22.24.29(33).30-nonaene. **L[7]**: 11.19-di(1*H*-5-indolylmethyl)-15-methyl-3.27-dioxa-11.15.19.33-tetraazatetracyclo-[27.3.1.O$^{4.9}$.O$^{21.26}$]tritiaconta-1(32).4(9).5.7.21(26).22.24.29(33).30-nonaene.



L[5]

Pale yellow oil. Amine: *N*,*N*-bis(3-aminopropyl)methylamine. Solvent: absolute ethanol. Yield 58%. IR (CsCl windows) ν(NH) (cm^{-1}): 3290, ν(C=C) and ν(C=N) (cm^{-1}): 1595, 1454. UV–vis spectrum (in CH_3CN) (λ(mn), ε((mol $L^{-1})^{-1}\cdot cm^{-1}$)): 266, 3595. ^1H NMR ($CDCl_3$) (ppm) δ: 7.78 (t), 1H, (Py); 7.6 (d), 2H, (Py); 7.4–6.7 (m), 8H, (C_6H_6); 5.0 (s) 4H, (Py-CH_2-O); 3.7 (m) 4H, (Ph-CH_2-NH); 2.5 (t), 4H, (-C$H_2$$CH_2$$CH_2$); 2.3 (t), 4H, (-$CH_2$$CH_2CH_2$); 1.5 (m), 4H, (-$CH_2$$CH_2$$CH_2$); 1.7 (s), 3H, (-$CH_3$). ^{13}C NMR ($CDCl_3$) (ppm) δ: 155.2, 155.1, 154.8, 154.5, 135.9, 129.0, 128.2, 127.3, 127.1, 126.8, 126.4, 119.5, 119.2, 110.3, 109.8, 69.3, 55.0, 54.9, 54.5, 54.3, 54.0, 53.8, 49.2, 46.3, 40.6, 39.6, 38.9, 29.3. FAB-MS (positive-ion) *m*/*z* (%): 461 ([L^5 + H]$^+$, 100), 921 ([2 + 2]$^+$, 10). Anal. calcd. for $C_{28}H_{36}N_4O_2\cdot 3H_2O$ (%): C 65.35, H 9.05, N 10.90; found: C 65.65, H 9.20, N 10.60.

The ligand is air stable and soluble in acetonitrile, absolute ethanol, chloroform, dimethylformamide, and dimethylsulfoxide. It is moderately soluble in dichloromethane and benzene and is insoluble in diethyl ether, petroleum ether, *n*-hexane, and water.

Synthesis of the scorpionand macrocycle L[3]

A fresh solution of L^1 (yellow oil) in absolute ethanol (75 cm^3) was refluxed during 30 min; an ethanolic solution of salicylaldehyde (1.02 mmol) was then added dropwise. The resulting solution, with an intense yellow colour, was refluxed with magnetic stirring for ca. 4 h. After cooling over ice, it was filtered off and reduced to dryness by rotary evaporation. The intense yellow oil obtained was dried under vacuum for 2 h.

L[3]

Yield 80%. Intense yellow oil. IR (CsCl windows) ν(OH) (cm^{-1}): 3412, ν(NH) (cm^{-1}): 3292, $\nu(C{=}N)_{imi}$ (cm^{-1}): 1630, ν(C=C) and ν(C=N) (cm^{-1}): 1597, 1455. UV–vis spectrum (in CH_3CN) (λ(mn), ε((mol $L^{-1})^{-1}\cdot cm^{-1}$)): 257, 12 444, 317, 2121. ^1H NMR (CD_3CN) (ppm) δ: 8.0 (s), 1H, (*H*C=N_{imi}); 7.6–6.6 (m), 15H, (aromatics); 4.9 (s) 4H, (Py-CH_2-O); 4.8 (s), 4H, (Ph-CH_2-NH); 3.5–3.4 (m), 12H, (-CH_2CH_2); 4.5 (sw), (-N*H*). ^{13}C NMR (CD_3CN) (ppm) δ: 166.4, 161.0, 160.9, 156.4, 156.3, 155.3, 138.1, 136.5, 133.3, 132.07, 131.3, 130.8, 129.6, 129.1, 126.6, 123.7, 121.1, 120.9, 120.3, 119.5, 118.1, 117.0, 112.6, 97.6, 69.9, 61.6, 59.0, 56.6, 55.7, 55.5, 48.7, 46.7, 45.7, 17.5. ^{13}C NMR DEPT-135 (CD_3CN) (ppm) (CH, CH_3) δ: 167.2, 138.9, 137.4, 134.0, 132.8, 132.3, 132.1, 130.3, 129.9, 121.8, 121.1, 120.3, 117.96, 117.5, 113.5, 112.8, 97.9, (CH_2) 71.5, 71.0, 62.2, 61.8, 57.4, 56.6, 53.9, 52.9, 51.9, 47.4, 46.0. FAB-MS (positive-ion) *m*/*z* (%): 566 ([L^3 + H]$^+$, 100), 461 ([L^3 – $CH_2N{=}CH(C_6H_4OH)$], 33). Anal. calcd. for $C_{34}H_{39}N_5O_3\cdot 3.5H_2O$ (%): C 65.90, H 7.30, N 11.30; found: C 65.85, H 7.45, N 10.60.

Synthesis of the di-pendant-armed macrocycles L[6] and L[7]

Four millimoles of freshly prepared 5-chloromethyl-4-methylimidazole hydrochloride or 3-chloromethylindole were mixed with triethylamine in 50 cm^3 of dry acetonitrile under a nitrogen atmosphere. The mixture was refluxed during 1 h. After the effervescence disappeared, 2 mmol of L^5 dissolved in 50 cm^3 of dry acetonitrile was slowly added. The reaction was then kept at 50 °C in a silicone bath during 5 days, with vigorous stirring and under the nitrogen atmosphere. After 5 days, the solution was filtered, and the filtrate was reduced to dryness. The crude product was then dissolved in water–chloroform and extracted with 3 × 25 cm^3 of $CHCl_3$. The organic phase was washed twice with 2 × 40 cm^3 of water and dried with anhydrous Na_2SO_4. The solution was then filtered and reduced to give an oil.

L[6]

Orange-yellow oil. Yield 26%. IR (CsCl windows) $\nu(NH)_{imid}$ (cm^{-1}): 3331, ν(C=C) and ν(C=N) (cm^{-1}): 1597, 1456. ^1H NMR ($CDCl_3$) (ppm) δ: 7.70 (t), 1H, (Py); 7.3 (d), 1H, (NHC*H*Nimid); 7.5–6.8 (m), 10H, (*Py*+C_6H_6); 5.1 (d) 4H, (Py-CH_2-O); 3.9 (d) 4H, (Ph-CH_2-N); 3.6 (d), 4H, (CH_2Imi); 2.6 (m), 4H, (-C$H_2$$CH_2$$CH_2$); 2.3 (m), 4H, (-$CH_2$$CH_2CH_2$); 1.8 (m), 4H, (-$CH_2CH_2$$CH_2$); 1.9 (s), 3H, (-C$H_3$); 1.6 (s), 3H, (-C$H_3$), 1.2 (s), 3H, (-C$H_3$). ^{13}C NMR ($CDCl_3$) (ppm) δ: 157.4, 157.1, 156.8, 156.6, 156.0, 155.7, 155.3, 139.0, 132.5, 132.0, 131.8, 130.7, 128.4, 127.2, 126,5, 124.4, 123.8, 123.6, 122,6, 122.4, 121.6, 119.9, 119.8, 113.8, 77.5, 71.6, 55.9, 54.9, 53.9, 47.4, 46.3, 41.5, 40.4, 29.7, 22.9, 22.2, 9.8, 8.9. MS (electrospray) *m*/*z* (%): 650 ([L^6 + H]$^+$, 35), 555 ([L^6 – ($C_5H_6N_2$)]$^+$, 25), 461 ([L^6 – 2($C_5H_6N_2$)]$^+$, 65). Anal. calcd. for $C_{38}H_{48}N_8O_2\cdot 2H_2O$ (%): C 66.65, H 7.65, N 16.35; found: C 66.65, H 7.70, N 16.65.

L[7]

Dark yellow oil. Yield 31%. IR (CsCl windows) $\nu(NH)_{indol}$ (cm^{-1}): 3408; $\delta(NH)_{indol}$ (cm^{-1}): 3266, ν(C=C) and ν(C=N) (cm^{-1}): 1596, 1454. ^1H NMR ($CDCl_3$) (ppm) δ: 7.9–6.8 (t), 21H, (aromatics); 5.3 (d), 4H, (Py-CH_2-O); 4.9 (s) 4H, (Ph-CH_2-N); 3.9 (d) 4H, (CH_2 . -Indol); 2.6–1.6 (m), 15H, (Aliphatics). ^{13}C NMR (CD_3CN) (ppm) δ: 169.2, 168.8, 168.6, 168.2, 149.7, 148.7, 142.7, 140.7, 140.4, 139.9, 139.2, 136.3, 133.5, 133.3, 133.2, 132.9, 132.8, 131.0, 130.8, 128.8, 124.2, 123.8, 123.5, 123.4, 90.3, 90.0, 89.9, 89.8, 89.3, 82.5, 82.2, 76.7, 76.4, 68.9, 68.2, 67.7, 62.2, 59.4, 53.6, 52.8, 38.8, 38.3, 33.9, 30.0, 27.1, 12.0. MS (electrospray) *m*/*z* (%): 720 ([L^7 + H]$^+$, 25), 590 ([L^7 – (C_9H_8N)]$^+$, 10), 461 ([L^7 – 2(C_9H_8N)]$^+$, 65). Anal. calcd. for $C_{46}H_{50}N_6O_2\cdot 3H_2O$ (%): C 71.50, H 7.30, N 10.85; found: C 71.65, H 7.75, N 10.90.

The ligands are air stable and soluble in acetonitrile, absolute ethanol, chloroform, dimethylformamide, and dimethylsulfoxide. They are moderately soluble in dichloromethane and insoluble in diethyl ether, petroleum ether, *n*-hexane, and water.

Synthesis of the metal complexes

Template reaction of Schiff-base macrocycles L[1] and L[4] in the presence of metal ions: General procedure for [ML][X]$_n$ (X = ClO_4^- or NO_3^-)

2,6-Bis(2-formylphenoxymethyl)pyridine (1 mmol) and $MX_n\cdot xH_2O$ (1 mmol) (M = Y(III), Ln(III), Zn(II), or Cd(II)) were dissolved in hot methanol or absolute ethanol (30 cm^3). A solution of *N*,*N*-bis(3-aminopropyl)methylamine or tris(2-aminoethyl)amine (1 mmol) in methanol or absolute ethanol

Table 1. Analysis, yield, and molar conductance (in CH_3CN) data for the complexes $[M_mL^{1-2-3}][X]_n \cdot xH_2O$.

						Elemental analysis (%)[a]					
M	L	*m*	*n*	*x*	X	C	N	H	Yield (%)	Λ_M/Ω^{-1} ($cm^2 \cdot mol^{-1}$)	Colour
(L^1 = $C_{27}H_{31}N_5O_2$)											
La	L^1	1	3	10	ClO_4^-	30.70 (30.20)	6.95 (6.50)	5.25 (4.80)	34	295	Yellow
Zn	L^1	1	2	4	ClO_4^-	41.05 (40.85)	9.10 (8.80)	5.20 (4.95)	35	125	Orange-yellow
Cd	L1	2	4	5	ClO_4^-	27.40 (27.70)	5.50 (5.95)	3.75 (3.50)	18	238	Yellow
(L^2 = $C_{27}H_{35}N_5O_2$)											
Y	L^2	1	3	2	NO_3^-	42.35 (42.00)	14.75 (14.50)	5.25 (5.10)	43	119	Pale yellow
La	L^2	1	3	5	NO_3^-	37.45 (37.00)	12.95 (12.80)	4.50 (5.15)	18	123	Pale yellow
Sm	L^2	1	3	6	NO_3^-	35.55 (35.80)	12.30 (12.35)	4.95 (5.20)	59	121	Pale yellow
La	L^2	1	3	9	ClO_4^-	30.00 (30.55)	6.60 (6.60)	4.80 (5.05)	25	222	Yellow
Ce	L^2	1	3	2	ClO_4^-	35.00 (34.65)	7.00 (7.50)	4.35 (4.20)	63	236	Yellow-gold
Gd	L^2	1	3	8	ClO_4^-	30.45 (30.55)	6.75 (6.60)	4.60 (4.85)	42	247	Pale yellow
Er	L^2	1	3	5	ClO_4^-	32.30 (31.90)	6.25 (6.85)	4.20 (4.45)	44	285	Yellow-orange
(L^3 = $C_{34}H_{39}N_5O_3$)											
Eu	L^3	1	3	7	NO_3^-	39.50 (39.65)	10.70 (10.90)	5.35 (5.20)	52	137	Yellow
Tb	L^3	1	3	6	NO_3^-	39.80 (40.10)	10.25 (10.95)	4.85 (5.05)	46	127	Dark yellow
La	L^3	1	3	5	ClO_4^-	37.90 (37.35)	6.40 (6.40)	5.00 (4.55)	47	277	Yellow
Pr	L^3	2	6	5	ClO_4^-	27.00 (26.60)	5.15 (4.55)	3.20 (3.20)	46	369	Yellow
Sm	L^3	1	3	7	ClO_4^-	35.80 (35.80)	6.20 (6.15)	5.15 (4.70)	56	284	Yellow
Zn	L^3	2	4	4	ClO_4^-	35.45 (35.00)	6.45 (6.00)	4.15 (4.05)	30	265	Yellow

[a]Required values are given in parentheses.

(25 cm^3) was added dropwise; magnetic stirring and heating was maintained during the addition. The solution was refluxed for 3 to 4 h, allowed to cool to room temperature, and then concentrated to ca. 15 cm^3. The complexes precipitated directly or after addition of diethyl ether (15 cm^3); they were filtered off and dried in vacuo. Microanalytical data are given in Tables 1 and 2. The complexes are air stable and soluble in acetone, dimethylformamide, methanol, acetonitrile, and dichloromethane. They are moderately soluble in chloroform and insoluble in water and absolute ethanol.

Direct synthesis between L^2, L^3, L^5, L^6, and L^7 and divalent and trivalent metal ions: General procedure for $[ML][X]_n$ (X = ClO_4^- or NO_3^-)

The appropriate metal salt $MX_n \cdot xH_2O$ (Y(III), Ln(III), Zn(II), or Cd(II) and X = NO_3^- or ClO_4^-) (0.50 mmol) was dissolved in methanol (for L^2, L^3, L^5, and L^7) or absolute ethanol (for L^6) (20 cm^3) and added to a solution of the ligand (0.50 mmol) in methanol (L^2, L^3, and L^5) or chloroform (L^6 and L^7) (50 cm^3). The mixture was stirred during 24–72 h at room temperature and cooled. When a precipitate did not developed immediately, the solution was partially concentrated under vacuum to give a solid, although in some cases the precipitation was aided by addition of some diethyl ether (ca. 5–10 cm^3). The products were filtered off, washed with cold absolute ethanol or methanol, and dried in vacuo.

Microanalytical data are given in Tables 1, 2, and 3. The complexes are air stable and are soluble in acetone, methanol, acetonitrile, and dichloromethane. They are moderately soluble in dimethylformamide and insoluble in chloroform, water, and absolute ethanol.

Results and discussion

Synthesis of the free ligands

We have previously reported that direct reaction between (**I**) with aliphatic or aromatic amines in the absence of template agents is a valid method to obtain Schiff-base and oxa-aza macrocyclic ligands (2, 19, 24). We now present seven macrocyclic ligands derived from this dicarbonyl precursor and two aliphatic diamines (mentioned in the starting material section) and the study of the complexation capacity of these ligands with a range of trivalent and divalent metal ions. Ligands L^1 and L^4 were obtained by reaction of (**I**) with both aliphatic diamines. These two macrocycles have already been reported in a previous paper (24).

Using L^1 and L^4 as the starting point, we have prepared five new macrocyclic ligands with different donor atom arrays (see Fig. 1). L^2 was synthesized by reduction of L^1, formed in situ using barium perchlorate, with sodium borohydride. In a similar way, L^5 was obtained from L^4. The pendant-armed macrocycle L^3 was obtained by a Schiff-base reaction between L^2 and salicylaldehyde, with formation of an iminic bond in the pendant arm. The ligands L^6 and L^7 were obtained by reaction of L^5 with 5-chloromethyl-4-methylimidazole hydrochloride and 3-chloromethylindole, respectively, following the method described in the experimental section.

We have found that the template approach is more effective for the preparation of L^2 and L^5, with yields of 64% and 58%, respectively. In previous papers, we have reported the effectiveness of a direct approach in the synthesis of large macrocycles, in which the presence of aromatic groups in

Table 2. Analysis, yield, and molar conductance (in CH_3CN for L^4 or in DMF for L^5) data for the complexes $[M_mL^{4-5}][X]_n{\cdot}xH_2O$.

						Elemental analysis (%)[a]					
M	L	*m*	*n*	*x*	X	C	N	H	Yield (%)	Λ_M/Ω^{-1} ($cm^2{\cdot}mol^{-1}$)	Colour
(L^4 = $C_{28}H_{32}N_4O_2$)											
Y	L^4	1	3	5	NO_3^-	40.45 (40.95)	12.20 (11.95)	5.05 (5.15)	53	158	Orange
La	L^4	2	6	—	NO_3^-	30.05 (30.40)	12.30 (12.65)	2.90 (2.90)	58	264	Orange
Nd	L^4	1	3	0.5	NO_3^-	42.25 (42.25)	11.50 (12.30)	4.50 (4.20)	87	144	Orange
Eu	L^4	1	3	—	NO_3^-	42.75 (42.35)	11.90 (12.35)	3.90 (4.05)	57	124	Orange
Ho	L^4	1	3	4	NO_3^-	38.80 (38.25)	11.05 (11.15)	5.00 (4.60)	91	137	Orange
Lu	L^4	1	3	2	NO_3^-	40.06 (39.40)	11.05 (11.50)	4.05 (4.25)	51	147	Orange
La	L^4	1	3	4	ClO_4^-	34.90 (34.80)	6.25 (5.80)	4.55 (4.15)	77	247	Yellow
Ce	L^4	1	3	4	ClO_4^-	34.85 (34.80)	6.33 (5.80)	4.10 (4.20)	35	232	Yellow
Er	L^4	1	3	1	ClO_4^-	36.30 (35.75)	6.50 (5.95)	4.00 (3.65)	49	224	Yellow
Zn	L^4	2	4	2	ClO_4^-	32.20 (32.90)	5.20 (5.50)	3.00 (3.55)	46	220	Yellow
Cd	L^4	1	2	4	ClO_4^-	40.20 (40.05)	7.05 (6.70)	4.70 (4.80)	51	158	Yellow
(L^5 = $C_{28}H_{36}N_4O_2$)											
Y	L^5	2	6	3	NO_3^-	31.55 (31.60)	12.85 (13.15)	4.10 (4.00)	22	143	Pale yellow
Eu	L^5	1	3	5	NO_3^-	37.95 (37.85)	10.60 (11.00)	4.75 (5.20)	62	72	Yellow
Tb	L^5	1	3	6	NO_3^-	37.20 (36.80)	11.15 (10.70)	4.90 (5.30)	36	67	Pale yellow
La	L^5	1	3	6	ClO_4^-	33.15 (33.40)	5.90 (5.60)	4.60 (4.80)	68	172	Yellow
Gd	L^5	1	3	3	ClO_4^-	34.90 (34.65)	5.85 (5.80)	4.20 (4.35)	39	179	Pale yellow
Zn	L^5	1	2	0.5	ClO_4^-	46.00 (45.80)	7.65 (7.65)	4.80 (5.10)	68	79	Yellow
Cd	L^5	2	4	—	ClO_4^-	31.40 (31.05)	5.70 (5.20)	3.25 (3.35)	43	67	Yellow

[a]Required values are given in parentheses.

Table 3. Analysis, yield, and molar conductance (in DMF for L^6 or in CH_3CN for L^7) data for the complexes $[M_mL^{6-7}][X]_n{\cdot}xH_2O$.

						Elemental analysis (%)[a]					
M	L	*m*	*n*	*x*	X	C	N	H	Yield (%)	Λ_M/Ω^{-1} ($cm^2{\cdot}mol^{-1}$)	Colour
(L^6 = $C_{38}H_{48}N_8O_2$)											
Y	L^6	2	6	5	NO_3^-	35.35 (35.40)	15.30 (15.20)	4.55 (4.55)	22	236	Yellow
Gd	L^6	2	6	4	NO_3^-	32.40 (32.45)	13.90 (13.95)	4.50 (4.00)	26	274	Yellow
La	L^6	1	3	7	ClO_4^-	37.70 (37.65)	9.35 (9.25)	5.30 (5.15)	31	240	Yellow
(L^7 = $C_{46}H_{50}N_6O_2$)											
La	L^7	2	6	7	ClO_4^-	32.00 (32.15)	5.25 (4.90)	4.10 (3.75)	63	365	Yellow
Zn	L^7	2	4	—	ClO_4^-	44.75 (44.30)	7.15 (6.75)	3.60 (4.05)	32	273	Yellow

[a]Required values are given in parentheses.

both organic precursors helps to minimize the formation of acyclic structures (19, 20). However, when the direct route was used to prepare L^2 and L^5, the aliphatic nature of the amine precursors seemed to increase the formation of undesired acyclic compounds, and low yields were obtained for both macrocycles. A template approach was thus chosen, and we have found that the use of barium(II) as the template agent increased the yields of the two macrocycles.

The FAB mass spectra for L^2, L^3, and L^5, as well as the electrospray mass spectra for L^6 and L^7, show the highest molecular weight peaks at *m*/*z* 462 (L^2), 566 (L^3), 461 (L^5), 650 (L^6), and 720 (L^7), corresponding to ($[L + H]^+$). The IR spectra feature the secondary amine N–H stretching band at ca. 3200–3292 cm^{-1} (in L^2, L^3, and L^5) or $\delta(NH)_{pyrrolic}$ at ca. 3330–3400 cm^{-1} (in L^6 and L^7). The spectra for L^2 and L^5 do not show bands in the 1620–1640 cm^{-1} region, where imine stretches are expected. The spectrum for L^3 features a band at ca. 1630 cm^{-1}, owing to the imine group present in the pendant arm. For L^7 it is possible to observe a band at ca. 3266 cm^{-1}, attributable to δ(NH) of the indole group.

The ^1H NMR spectra in CD_3CN (for L^2 and L^3) and in $CDCl_3$ (for L^5, L^6, and L^7) confirm the integrity of the ligands in solution. The ^{13}C NMR spectra for L^2, L^5, L^6, and L^7 feature 27, 28, 38, and 46 signals, respectively, one for each C in the macrocyclic skeleton. This suggests that both the reduction of the imine bonds and the presence of the pendant arms lead to an increase in the ligand flexibility and unsymmetrical behaviour of the ligands. UV–vis spectra in acetonitrile were recorded for L^2, L^3, and L^5. The broad absorption bands observed at 269 nm for L^2, at 257 and 317 nm for L^3, and at 266 nm for L^5 can be attributed to the π–π* transitions of the pyridine and phenyl groups.

Metal complexes: Microanalytical and molar conductivity data

Yttrium and lanthanide trivalent metal ions and divalent zinc and cadmium have been used to explore the coordination behaviour of this new family of oxa-aza macrocycles. Condensation between 2,6-bis(2-formylphenoxymethyl)pyridine and tris(2-aminoethyl)amine (L^1) or *N*,*N*-bis(3-aminopropyl)methylamine (L^4) in the presence of the corresponding hydrated metal salt, in a 1:1:1 molar ratio, leads to the formation of mononuclear complexes formulated as $[LaL^1](ClO_4)_3 \cdot 10H_2O$, $[ZnL^1](ClO_4)_2 \cdot 4H_2O$, and $[ML^4](X)_n \cdot xH_2O$ (M = Y(III), Ce(III), Nd(III), Eu(III), Ho(III), Er(III), Lu(III), and Cd(II); X = NO_3^- or ClO_4^-) and dinuclear complexes formulated as $[Cd_2L^1](ClO_4)_4 \cdot 5H_2O$ and $[M_2L^4](X)_n \cdot xH_2O$ (M = La(III); X = NO_3^- and M = Zn(II); X = ClO_4^-). Microanalytical data for these complexes are shown in Table 1 (L^1) and Table 2 (L^4).

Only complexes with trivalent metal ions have been obtained with L^2, with the formula $[ML^2](X)_3 \cdot xH_2O$ (M = Y(III), La(III), Ce(III), Sm(III), Gd(III), and Er(III); X = ClO_4^- or NO_3^-). Reaction between L^5 and Y(III), La(III), Gd(III), Eu(III), Tb(III), Zn(II), and Cd(II) leads to the formation of mononuclear complexes, formulated as $[ML^5](X)_n \cdot xH_2O$ (M = La(III), Eu(III), Gd(III), Tb(III), and Zn(II); X = ClO_4^- or NO_3^-), as well as the dinuclear complexes $[M_2L^5](X)_n \cdot xH_2O$ (M = Y(III); X = NO_3^- and M = Cd(II); X = ClO_4^-). Microanalytical data for these complexes are shown in Table 1 (L^2) and Table 2 (L^5). The syntheses were also attempted with the perchlorates of Zn(II) and Cd(II) for L^2, as well as the nitrates of La(III) and the perchlorates of Ce(III) and Eu(III) for L^5; however, with these metals only species with unsatisfactory analytical data were obtained.

A direct method has been successfully used to synthesize complexes with L^3. Reaction of freshly prepared L^3 in the presence of the corresponding metal salt yielded mononuclear complexes of formula $[ML^3](X)_3 \cdot xH_2O$ (M = La(III) and Sm(III); X = ClO_4^-; M = Eu(III) and Tb(III); X = NO_3^-) (see Table 1) and the dinuclear complexes $[Pr_2L^3](ClO_4)_6 \cdot 5H_2O$ and $[Zn_2L^3](ClO_4)_4 \cdot 4H_2O$. Under the experimental conditions employed, it has been impossible to isolate the expected metal complexes with the nitrates of Y(III) and La(III) and with the perchlorate of Cd(II).

The reaction between equimolar amounts of freshly prepared L^6 and L^7 and the perchlorates of La(III) and Zn(II), as well as the nitrates of Y(III) and Gd(III), gave analytically pure products of formula $[LaL^6](ClO_4)_3 \cdot 7H_2O$, $[M_2L^6](NO_3)_6 \cdot xH_2O$ (M = Y(III) and Gd(III)), and $[M_2L^7](ClO_4)_n \cdot H_2O$ (M = La(III) and Zn(II)). The presence of extra donor atoms in the pendant arms leads to the formation of binuclear species with the majority of the metal ions employed. The syntheses were also attempted using the perchlorate of Cd(II) and the nitrates of Eu(III) and Tb(III), but only a mixture of unreacted metal salt and free ligand were recovered.

In the absence of crystal structures, which are decisive in the elucidation of the coordinative environment of the metal ions in these molecules, it is difficult to give an appropriate explanation for the formation, depending on the ligand and the metal ion, of di- or mononuclear complexes. Reaction with Cd(II) and Zn(II) yields dinuclear complexes in most cases, probably because of the small size of both ions when compared with the lanthanide(III) cations. It is also noteworthy that the increase in the flexibility and complexity of the ligands, from L^1 to L^3 and from L^4 to L^6 or L^7, does not appear to affect especially the formation of the corresponding complexes.

Molar conductivity data, measured at room temperature using DMF or acetonitrile solutions, show the ionic nature of all complexes in these solvents. The values are in accordance with those expected for 1:1 or 1:2 electrolytes (for complexes with L^1, L^2, L^3, L^4, and L^5) or for 1:2 or 1:3 electrolytes (L^6 and L^7 complexes) (26). The value for the complex $[Pr_2L^3](ClO_4)_6 \cdot 5H_2O$, measured in acetonitrile, falls between the ranges reported for 1:2 and 1:3 electrolytes. Data for the different complexes are given in Tables 1, 2, and 3. Molar conductivities were measured again 1 week after sample preparation for the complexes containing L^2, L^5, and L^6; a significant increase in the values was observed in some complexes, suggesting the displacement of counter ions from the coordination sphere by solvent molecules (26).

Metal complexes: FAB and electrospray mass spectra

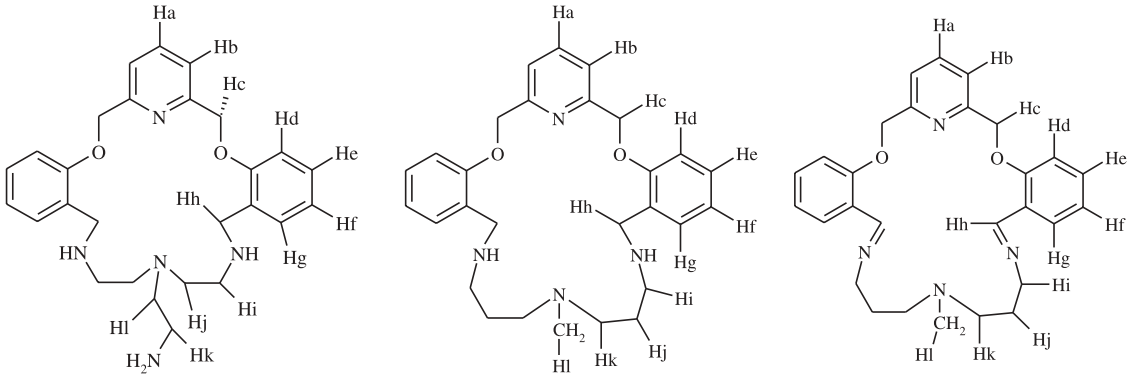
All mass spectra feature peaks attributable to the corresponding macrocyclic ligand, confirming the stability of the seven macrocycles in their metal complexes. Moreover, the spectra show peaks at higher molecular weights, which in some cases have also been assigned. The spectra for the complexes with L^1 contain peaks attributable to $[ML^1]^+$ (M = La(III) and Cd(II)) and $[ZnL^1(ClO_4)]^+$. For the complexes with L^2, the spectra show peaks assignable to the fragments $[ML^2(ClO_4)]^+$ (M = La(III) and Ce(III)), and $[L^2(ClO_4)]^+$ and $[LaL^2(NO_3)]^+$ are present. In the case of the L^3 complexes, peaks assignable to the fragments $[ML^3(ClO_4)]^+$ (M = La(III), Pr(III), Sm(III) and Zn(II)), $[ML^3(NO_3)]^+$ (M = Eu(III)), and $[ML^3]^+$ (M = Eu(III) and Sm(III)) can be observed.

The spectrum of the dinuclear nitrate La(III) complex with L^4 contains peaks corresponding to the fragments $[La_2L^4(NO_3)_3]^+$ and $[LaL^4(H_2O)]^+$. The mononuclear Ce(III), La(III), and Nd(III) complexes exhibit peaks due to the species $[ML^4(ClO_4)_2]^+$ (M = La(III) and Ce(III)) and $[NdL^4(NO_3)]^+$, confirming the presence of the metal ions in the complexes. Peaks attributable to the fragment $[L^4(ClO_4)]^+$ are also present in the spectra of the complexes with Ce(III) and Cd(II). For the complexes with L^5, the mass spectra feature peaks assignable to the fragments $[ML^5(NO_3)_2]^+$ (M = Y(III), Eu(III), and Tb(III)), $[ML^5(ClO_4)]^+$ (M = La(III), Gd(III), Zn(II), and Cd(II)), and $[ML^5]^+$ (M = Y(III) and Zn(II)). The FAB mass spectra for the L^6 complexes show peaks assignable to the fragments $[ML^6]^+$ and $[L^6(NO_3)_2]^+$, while for the L^7 complexes, peaks corresponding to the fragments $[LaL^7]^+$ and $[ZnL^7(H_2O)]^+$ can be observed.

Infrared spectra

The IR spectra for the complexes with L^1, L^2, L^4, and L^5 confirm the cyclic nature of the ligands in their metal complexes. The spectra for the complexes with L^1 and L^4 show a band at ca. 1639–1660 cm^{-1}, attributable to the imine groups, and no bands due to ν(C=O) vibrations. In the Cd(II) complex with L^1, a band at ca. 3227 cm^{-1}, attributable to

Fig. 2. ^{1}H NMR data (300 MHz) for $[LaL^2](ClO_4)_3\cdot 9H_2O$ (in CD_3CN), $[LaL^5](ClO_4)_3\cdot 6H_2O$ (in $CDCl_3$), and $[La_2L^4](NO_3)_6$ (in DMSO-d_6).



L^2 **L^5** **L^4**

$\nu(NH_2)$, is also observed (27). The spectra exhibit medium to strong bands at ca. 1603–1597 and 1458 cm^{-1}, as expected for the $\nu(C{=}C)_{ar}$ and $\nu(C{=}N)_{py}$ ring vibrations (28). The $\nu(C{=}N)_{py}$ band, as well as those corresponding to the imine groups, are generally shifted to higher wave numbers when compared with those of the free ligands, suggesting coordination via nitrogen atoms (29, 30). The IR spectral results for the complexes with L^3 confirm that the imine group is present in the pendant arm of the ligand, showing an intense band at ca. 1630–1650 cm^{-1} that is attributable to $\nu(C{=}N)$ and no bands due to $\nu(C{=}O)$ and $\nu(NH_2)$ groups (27). The bands attributable to $\nu(NH)$ in the complexes of L^2, L^3, and L^5 cannot be observed because of the existence of a broad band at ca. 3380–3520 cm^{-1}, assignable to the stretching and bending modes of water (31). For the complexes with L^2 and L^5, the absence of bands at ca. 1620–1660 cm^{-1} in the spectra confirms the reduction of the iminic groups.

The IR spectra of the complexes with L^6 and L^7 also contain absorption bands characteristic of the ligand frameworks. The sharp absorption band occurring in the region 3340–3060 cm^{-1} is attributable to $\nu(NH)$ of the indole or imidazole groups. For the complexes of L^6, the band at ca. 1648 cm^{-1} can be assigned to the $\delta(NH)$ of the imidazole groups. Bands at ca. 1602 and 1458 cm^{-1}, corresponding to the aromatic ring vibrations, are also present. These bands are shifted to lower energy when compared with their position in the spectra of the free ligands, probably because of coordination to the metal ion.

The absorptions of the counter-ions provide some useful structural information. The IR spectra for all nitrate complexes show bands at ca. 1448–1460 (ν_5), 1300 (ν_1), and 1030 (ν_2) cm^{-1}, suggesting the existence of coordinated nitrate groups, as well as a band at ca. 1384 cm^{-1}, attributable to the presence of ionic NO_3^- (32, 33). Although the spectra do not allow a clear-cut difference between mono- and bidentate chelating nitrates, the separation between ν_5 and ν_1 (ca. 160 cm^{-1}) suggests the presence of nitrate groups acting as bidentate (34, 35). Regarding the perchlorate complexes, bands attributable to the asymmetric Cl–O stretching mode at ca. 1088 cm^{-1} (ν_3) and the asymmetric Cl–O bending mode (ν_4) at ca. 625 cm^{-1} can be observed. The highest energy band consists in three well-resolved maxima at ca. 1121, 1115, and 1088 cm^{-1}; the ν_4 band also shows splitting with maxima at ca. 636 and 626 cm^{-1} (36). The splitting of these bands is indicative of coordination of at least one perchlorate anion to the metal.

NMR spectra

The ^{1}H NMR spectra of some diamagnetic complexes with Y(III), La(III), and Zn(II) were recorded immediately after dissolution in CD_3CN, DMSO-d_6, or CD_3OD at room temperature. The spectra of the complexes $[LaL^1](ClO_4)_3\cdot 10H_2O$ and $[ZnL^1](ClO_4)_2\cdot 4H_2O$ (in CD_3CN) are complicated, showing more signals than expected. This may be indicative of the following: (*i*) the co-existence of additional processes in solution such as dimerization; (*ii*) the existence of demetallation processes in solution or geometric changes; and (or) (*iii*) the hydrolysis of the iminic groups. We ran the spectra at the following different temperatures: 298.15, 313.15, and 323.15 K. In all cases the number of signals never decreased notably, suggesting slow intersystem changes. The complexes $[LaL^2](ClO_4)_3\cdot 9H_2O$ and $[La_2L^4](NO_3)_6$ (in DMSO-d_6) and $[LaL^5](ClO_4)_3\cdot 6H_2O$ (in CD_3CN) gave the expected simple spectra, indicating the integrity of the complexes in those solvents (see Fig. 2, Table 4).

The spectra of the complexes $[LaL^3](ClO_4)_3\cdot 5H_2O$, $[YL^4](NO_3)_3\cdot 5H_2O$, $[Zn_2L^4](ClO_4)_4\cdot 2H_2O$, and $[LaL^4](ClO_4)_3\cdot 4H_2O$ (in CD_3CN) are complicated and show more signals than expected (complex and free ligand signals), which may be indicative of the existence of demetallation processes in solution or dimerization reactions in the dinuclear complexes. Nevertheless, clear peaks at δ 9.20, 8.60, 9.00, and 9.20 ppm, corresponding to the imine protons in the ligands, are present. The ^{1}H NMR spectra of $[Y_2L^6](NO_3)_6\cdot 5H_2O$ and $[LaL^6](ClO_4)_3\cdot 7H_2O$ (in DMSO-d_6) are also complicated, maybe because of the nonsymmetric topology of the ligand. Nevertheless, clear peaks at δ 7.8 and 8.8 ppm, corresponding to the aromatic imidazol protons of the pendant arms, as well as the signals attributable to aromatic rings of the macrocycle (37), confirm the integrity of the ligand L^6 in both metal complexes.

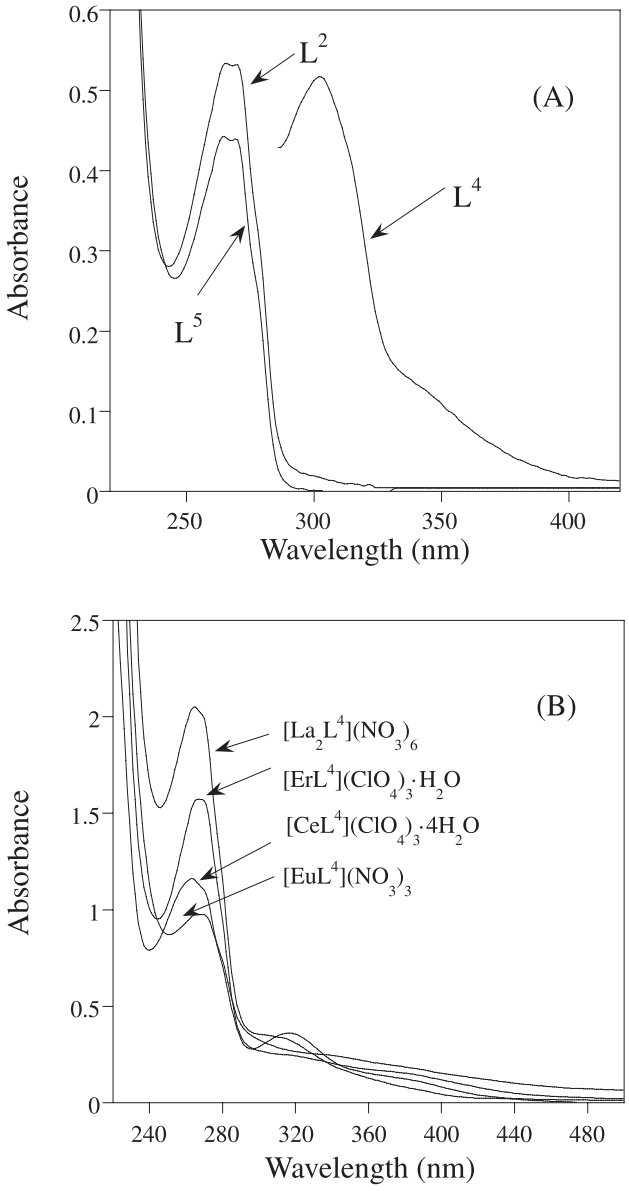
Electronic absorption spectra

The electronic spectra for L^2, L^3, L^4, and L^5, as well as some of their corresponding metal complexes, were recorded at room

Table 4. ^{1}H NMR data for the complexes $[LaL^2](ClO_4)_3\cdot 9H_2O$ and $[La_2L^4](NO_3)_6$ (in DMSO-d_6) and $[LaL^5](ClO_4)_3\cdot 6H_2O$ (in CD_3CN).

	δ integration (ppm)		
Assignment	$[LaL^2](ClO_4)_3\cdot 9H_2O$	$[LaL^5](ClO_4)_3\cdot 6H_2O$	$[La_2L^4](NO_3)_6$
Ha	7.9 (t) — 1H	7.8 (t) — 1H	7.9 (t) — 1H
Hb, Hd–Hg	7.7–6.8 (m) — 10H	8.5–6.8 (m) — 10H	7.7–6.9 (m) — 10H
Hc	5.2 (s) — 4H	5.4 (s) — 4H	5.5 (s) — 4H
Hh	4.2 (s) — 4H	4.2 (s) — 4H	8.3 (s) — 2H
Hi, Hj, Hk, Hl	3.0–2.6 (m) — 12H	3.1–1.0 (m) — 15H	2.5–1.5 (m) — 15H

Fig. 3. Electronic spectra for L^2, L^4, and L^5 (A) and some ML^4 complexes (B) in acetonitrile solution. [L] = [ML] = 9.0 E^{-5} mol L^{-1}.



temperature in acetonitrile solutions. The spectra for the reduced ligands L^2 and L^5 present one band at ca. 269–266 nm (ε ≈ 5344 and 3595 $mol^{-1}\cdot L\cdot cm^{-1}$, respectively). The Schiff base ligands L^3 and L^4 exhibits two bands, at ca. 257 nm (ε ≈ 12 444 $mol^{-1}\cdot L\cdot cm^{-1}$) and ca. 317 nm (ε ≈ 2921 $mol^{-1}\cdot L\cdot cm^{-1}$) for L^3 and at ca. 303 nm (ε ≈ 16 066 $mol^{-1}\cdot L\cdot cm^{-1}$) and ca. 351 nm (ε ≈ 5930 $mol^{-1}\cdot L\cdot cm^{-1}$) for L^4. In all cases, these bands are associated with the π–π* and *n*–π* electronic transitions in the chromophores — pyridine and phenyl rings — that are present in the macrocyclic skeletons (38).

The UV–vis spectra for some Y(III), Ln(III), and Zn(II) nitrate and perchlorate complexes of L^2 and L^4 exhibit two or three absorption bands in the regions 262–270, 315–325, and 370–385 nm. The shift in the absorption maxima that is observed when it is compared with those of the free macrocycles may be due to the presence of the metal in the species and could be attributable to the π–π* and *n*–π* transitions of the coordinated macrocycles. In some cases, the intensity of the absorption bands changed slightly when the spectra were recorded after 1 and 2 weeks, suggesting the displacement of some coordinated anions or water molecules by acetonitrile molecules. The spectral data for the complexes are given in Table 5, and the electronic spectra for the free ligands L^2, L^4, and L^5 and some ML^4 metal complexes are shown in Fig. 3.

Fluorescence emission spectra

Room-temperature emission spectra were registered using 10^{-5}–10^{-6} mol L^{-1} acetonitrile solutions for the Eu(III), Tb(III), and Zn(II) complexes with L^3, L^4, and L^5. Unfortunately, no emission could be detected in these complexes, probably because of (*i*) the presence of water molecules in the complexes; (*ii*) the presence of free uncoordinated amines with the lone-pair unoccupied; and (*iii*) the coexistence of nonradiative mechanisms that quenched the emission, in a similar way to those reported for other macrocycle ligands derived from similar aliphatic or aromatic precursor (2, 19, 24, 39).

Conclusions

Seven [1+1] oxa-aza macrocyclic ligands, five of them new, have been prepared using 2,6-bis(2-formylphenoxymethyl)pyridine as the precursor. Treatment of the previously reported Schiff-base macrocycles L^1 and L^4 with $NaBH_4$, in the presence of Ba(II) as a template agent, gave the corresponding reduced macrocycles L^2 and L^5. The more sophisticated ligands L^3, L^6, and L^7, provided with pendant arms, have been synthesized by condensation or alkylation reactions with the amine groups present in L^2 and L^5. Complexes with these seven ligands have been prepared by template reaction or direct methods, using the nitrates and (or) perchlorates of Y(III), Ln(III), Cd(II), or Zn(II) ions.

The complexes are mono- or dinuclear, depending on the macrocyclic ligand and (or) metal salt employed. Although

Table 5. UV–vis spectral data for the complexes with L^2 and L^4 in acetonitrile solution at room temperature.

Complexes	λ (nm); ε ((mol L^{-1})$^{-1}$·cm^{-1})
$[YL^2](NO_3)_3·2H_2O$	264 (9071); 312(*sh*) (3065)
$[LaL^2](NO_3)_3·5H_2O$	266 (8528); 316(*sh*) (3113)
$[SmL^2](NO_3)_3·6H_2O$	266 (6778)
$[LaL^2](ClO_4)_3·9H_2O$	267 (6796)
$[CeL^2](ClO_4)_3·2H_2O$	268(11249); 322(*sh*) (2559)
$[GdL^2](ClO_4)_3·8H_2O$	268 (7770)
$[ErL^2](ClO_4)_3·5H_2O$	267 (7298)
$[YL^4](NO_3)_3·5H_2O$	266 (8468); 319(*sh*) (3257)
$[La_2L^4](NO_3)_6$	266 (5313); 313(*sh*) (1744)
$[EuL^4](NO_3)_3$	268 (4602); 339(*sh*) (999); 385(*sh*) (704)
$[LuL^4](NO_3)_3·2H_2O$	267 (9871); 323(*sh*) (2355)
$[LaL^4](ClO_4)_3·4H_2O$	256 (10940); 316 (4426); 384(*sh*) (1102)
$[CeL^4](ClO_4)_3·4H_2O$	268 (10202); 320(4862); 379(*sh*) (401)
$[ErL^4](ClO_4)_3·H_2O$	267 (5902); 324(4842); 379(*sh*) (527)
$[Zn_2L^4](ClO_4)_4·2H_2O$	269 (7282); 335(*sh*) (4347)

Note: [Complex] = 10^{-4}–10^{-6} mol L^{-1}; *sh* = shoulder.

it is not possible to establish any clear link between the formation of mono- or dinuclear species and the size of the cation employed, it is worth mentioning that reaction with Cd(II) and Zn(II) generally generates the dinuclear complex, suggesting that the macrocyclic cavity in L^1, L^3, L^4, and L^5 is large enough to accommodate two of these metal cations. The complexes obtained with L^6 and L^7, provided with two lateral pendant arms, are always dinuclear except in one case, suggesting that the increase in the number of donor atoms present in the macrocyclic skeleton facilitates the formation of dinuclear compounds and showing the ability of these two macrocycles to host two metal ions.

Acknowledgements

Work supported in part by Xunta de Galicia (PGIDT01PXI20901PR) (Spain) and the European Community's Human Potential Programme under contract HPRN-CT-2000-00029 (Molecular Level Devices and Machines). C.L. acknowledges the financial support provided through the European Community's Human Potential Programme under contract HPRN-CT-2000-00029 (Molecular Level Devices and Machines).

References

1. K. Campbell, R. McDonald, M.J. Fergusson, and R.R. Tykwinski. Organometallics, **22**(7), 1353 (2003).
2. C. Lodeiro, R. Bastida, E. Bértolo, A. Macías, and A. Rodríguez. Trans. Met. Chem. **28**, 388 (2003).
3. R.J.A. Janssen, L.F. Lindoy, O.A. Mattews, G.V. Meehan, A.N. Sobolev, and A.H. White. J. Chem. Soc. Chem. Commun. 735 (1995).
4. D.E. Fenton and B.A. Nájera. J. Coord. Chem. **54**, 239 (2001).
5. H. Adams, R. Bastida, D.E. Fenton, A. Macías, S.E. Spey, and L. Valencia. J. Chem. Soc. Dalton Trans. 4131 (1999).
6. L. Valencia, R. Bastida, M. López-Deber, A. Macías, A. Rodríguez, and M. Vicente. Z. Anorg. Allg. Chem. **629**(2), 268 (2003).
7. M. Kanesato, H. Houjou, Y. Nagawa, and K. Hiratani. Inorg. Chem. Commun. **5**(11), 984 (2002).
8. K.P. Balakrishnan, H.A.A. Omar, P. Moore, N.W. Alcok, and G.A. Pike. J. Chem. Soc. Dalton Trans. 2965 (1999).
9. S.J. Grant, P. Moore, H.A.A. Omar, and N.W. Alcock. J. Chem. Soc. Dalton Trans. 485 (1994).
10. K.R. Adam, L.F. Lindoy, B.W. Skelton, S.V. Smith, and A.H. White. J. Chem. Soc. Dalton Trans. 3361 (1994).
11. M. Raidt, M. Neuburger, and T.A. Kaden. Dalton Trans. **7**, 1292 (2003).
12. K.P. Wainwright. Applications of polyaza macrocycles with nitrogen-attached pendant arms. *In* Advances in inorganic chemistry. Vol. 52. *Edited by* A.G. Sykes. Academic Press, San Diego. 2001. p. 293.
13. S. Aime, E. Gianolio, D. Corpillo, C. Cavalloti, G. Palmisano, M. Sisti, G.B. Giovenzana, and R. Pagliarin. Helv. Chim. Acta, **86**(3), 615 (2003).
14. S.K. Sengupta, O.P. Pandey, A. Sinha, and S. Tripathi. Prog. Cryst. Growth Charact. Mater. **45**(1–2), 37 (2002).
15. F. Benetollo, G. Bombieri, A.M. Adeyga, K.K. Fonda, W.A. Gootee, K.M. Samaria, L.M. Vallarino. Polyhedron, **21**(4), 425 (2002).
16. J. Costamagna, G. Ferraudi, B. Matsuhiro, M. Campos-Vallette, J. Canales, M. Villagran, J. Vargas, and M.J. Aguirre. Coord. Chem. Rev. **196**, 125 (2000).
17. X. Chen, D.M. Du, and W.T. Hua. Tetrahedron Asymmetry, **14**(8), 999 (2003).
18. P.W. Smet, T.F. Pauwels, and P.J. Dierickx. Hum. Exp. Toxicol. **21**(8), 421 (2002).
19. C. Lodeiro, R. Bastida, A. De Blas, D.E. Fenton, A. Macías, A. Rodríguez, and T. Rodríguez-Blas. Inorg. Chim. Acta, **267**, 55 (1998).
20. M. Vicente, C. Lodeiro, H. Adams, R. Bastida, A. de Blas, D.E. Fenton, A. Macías, A. Rodríguez, and T. Rodríguez-Blas. Eur. J. Inorg. Chem. 1015 (2000).
21. M. Vicente, R. Bastida, C. Lodeiro, A. Macías, A.J. Parola, L. Valencia, and S.E. Spey. Inorg. Chem. **42**(21) 6768 (2003).
22. N.A. Bailey, D.E. Fenton, S.J. Kitchen, T.H. Lilley, M.G. Williams, P.A. Tasker, A.J. Tasker, and L.F. Lindoy. J. Chem. Soc. Dalton Trans. 627 (1991).
23. R. Turner, C.F. Huebner, and C.R. Scholz. J. Am. Chem. Soc. **71**, 2801 (1949).
24. C. Lodeiro, R. Bastida, E. Bértolo, A. Macías, and A. Rodríguez. Polyhedron, **22**, 1701 (2003).
25. P.G. Grimsley, L.F. Lindoy, H.C. Lip, R.J. Smith, and J.T. Baker. Aust. J. Chem. **30**(9), 2095 (1977).
26. W.J. Geary. Coord. Chem. Rev. **7**, 81 (1971)
27. S.C. Cummings and D.H. Bush. J. Am. Chem. Soc. **92**, 1924 (1970)
28. S.M. Peng, G.C. Gordon, and V.L. Goedken. Inorg. Chem. **17**(1), 119 (1970).
29. N.S. Gill, R.H. Nuttall, and D.E. Scaife. J. Inorg. Nucl. Chem. **18**, 79 (1961).
30. S. Aime, M. Botta, U. Casellato, S. Tamburini, and P.A. Vigato. Inorg. Chem. **34**(23), 5825 (1995).
31. K. Nakamoto. Infrared and raman spectra of inorganic and coordination compounds. 5th ed. Wiley Interscience, New York. 1997.
32. N.F. Curtis and Y.M. Curtis. Inorg. Chem. **4**(6), 804 (1965).
33. A.B.P. Lever, E. Mantovan, and B.S. Ramaswam. Can. J. Chem. **49**(11), 1956 (1971).
34. V.A.J. Aruma and V. Alexander. Inorg. Chim. Acta, **249**, 93 (1996).
35. W. Radecka-Paryzek. Inorg. Chim. Acta, **109**(3), L21 (1985).

36. L. Decola, D.L. Smailes, and L.M. Vallarino. Inorg. Chem. **25**, 1729 (1986).
37. M. Di Vaira, F. Mani, M. Menicatti, P. Stoppioni, and A. Vacca. J. Chem. Soc. Dalton Trans. 661 (1997).
38. E. Pretsch, T. Clerc, J. Seibl, and W. Simon. Tables of spectral data for structure determination of organic compounds. 2nd. ed. Springer-Verlag, Berlin-Heidelberg. 1989.
39. C. Bazzicalupi, A. Bencini, A. Bianchi, C. Giorgi, V. Fusi, B. Valtancoli, M.A. Bernardo, and F. Pina. Inorg. Chem. **38**(17), 3806 (1999).